Residence Time Analysis of Rare-Gas Atoms Trapped at a Solid Surface

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Recently a model based on an attractive square well and impulsive repulsive potential between a gas and a solid surface has been employed to estimate the fraction of gas atoms trapped in the potential well at the solid surface.[1] A gas atom was considered trapped if it transferred enough energy to the solid (as judged by the thermal accommodation coefficient) to fall into the potential well, i.e., to have negative total energy where the zero of energy is assumed to be the infinitely separated gas atom and solid with the gas atom at rest.[1] The criterion for gas trapping when considering experimental scattering data has been the assumption that the trapped gas is emitted from the surface with a random (cosine) distribution.[2] To assess the possibility that rare-gas atoms may fall into the interatomic well with the metal surface (i.e., be trapped according to the definition of Ref. 1) and still be re-emitted from the surface in a nonrandom distribution, some estimates of surface residence times for the gas should be made. If such a phenomenon as suggested above were to occur, then the calculated trapping probability of the square well model[1] would be expected to be larger than those found experimentally, as has been observed to be the case for krypton and xenon interactions with a tungsten (110) surface.[2] The idea that a gas particle may execute several vibrations at a surface and still not reach thermodynamic equilibrium is not a new one.[3] In this paper the pertinent theory describing this effect is presented, and empirical calculations estimating the magnitude of the effect are presented.

The equation giving the mean residence time τ_a in the interatomic potential well may be written as

$$\tau_a=[(n+1)\nu]^{-1}\exp(E_d/kT_s) \quad n=0,\ 1,\ 2,\ \text{and}\ 3, \tag{1}$$

where ν is the fundamental vibrational frequency of the trapped-atom–surface-atom complex and E_d is the activation energy for reemission ("desorption") which is measured as the positive difference in energy between the vacuum level and the occupied level in the potential well. The first task is clearly to obtain values for the vibrational frequencies of the various tungsten–rare-gas complexes. In order to do this, it is useful to recall the data of McCarroll and Ehrlich[4] who report that the ratio of the force constant for a tungsten–xenon complex to that of diatomic tungsten is given by

$$k_{\mathrm{W-Xe}}/k_{\mathrm{W-W}}=0.03. \tag{2}$$

The definition of the fundamental vibrational frequency is given by

$$\nu_{ij}=(1/2\pi)\,(k_{ij}/\mu_{ij})^{\frac{1}{2}}, \tag{3}$$

where k_{ij} is the force constant of the ij vibration in the harmonic oscillator approximation, and μ_{ij} is the reduced mass of the ij complex, i.e.,

$$\mu_{ij}=m_im_j/(m_i+m_j), \tag{4}$$

when the masses of species i and j are given by m_i and m_j, respectively.

Another useful expression relating the various force constants to the interatomic potential well depths is the following[5]:

$$k_{ij}=k_{il}(D_{ij}/D_{il}), \tag{5}$$

where D is the depth of the interatomic potential well.[1] Equation (5) may be used to evaluate the ratio of two of the tungsten–rare-gas atom force constants provided values of the well depths are known (and since $k_{\mathrm{W-Xe}}/k_{\mathrm{W-W}}$ is known to be 0.03). If the ratio of force constants is known, then the ratio of vibrational frequencies may be found from Eq. (3) as follows:

$$\frac{\nu_{\mathrm{W-W}}}{\nu_{\mathrm{W}-i}}=\left[\frac{\mu_{\mathrm{W}-i}}{\mu_{\mathrm{W-W}}}\times\frac{k_{\mathrm{W-W}}}{k_{\mathrm{W}-i}}\right]^{\frac{1}{2}}, \tag{6}$$

where i represents a rare-gas atom. The results of the above calculations are summarized in Table I along with several other relevant parameters.

It is possible to estimate $\nu_{\mathrm{W-W}}$ from the relation

$$h\nu_{\mathrm{W-W}}=k\theta_{\mathrm{D,sur}}, \tag{7}$$

TABLE I. Parameters of calculation of residence time of rare-gas atoms in the gas–solid potential well.

$i\equiv$rare gas	$D_{\mathrm{W}-i}$ (cal/mole)	$k_{\mathrm{W}-i}/k_{\mathrm{W-W}}$	$\nu_{\mathrm{W-W}}/\nu_{\mathrm{W}-i}$	$\nu_{\mathrm{W}-i}\times10^{-11}$ (sec^{-1})	$h\nu_{\mathrm{W}-i}$ (cal/mole)
He	150	5.29×10^{-4}	8.98	4.87	46.5
Ne	500	1.76×10^{-3}	10.60	4.12	39.3
Ar	1900	6.71×10^{-3}	7.30	5.98	57.0
Kr	4250	0.015	6.47	6.75	64.4
Xe	8500	0.03	5.27	8.28	79.0

TABLE II. Reemission parameters of average rare-gas atom of krypton or xenon trapped at a tungsten surface with $T_g = 295$ K.

Gas	T_s (°K)	E_d (cal/mole)	n	$\tau_a \times 10^{14}$ (sec)	N (cycles)
Kr	375	359	60	3.92	1.60
	575	265	61.3	3.01	1.26
	775	172	62.8	2.61	1.12
Xe	375	2362	77.2	36.20	23.3
	575	2217	79.0	10.38	6.84
	775	2072	80.8	5.66	3.81

where h and k are the Planck and Boltzmann constants, respectively, and $\theta_{D,sur}$ is the surface Debye temperature. The latter quantity is empirically found to be $\sim 50\%$–75% of the bulk Debye temperature.[6,7] It will be assumed here that $\theta_{D,sur} = \frac{2}{3}(315) = 210$ K. From Eq. (7) this gives a value of ν_{W-W} of 4.37×10^{12} sec^{-1}. Thus, values of ν_{W-i} may be calculated from Eq. (6), and these results are also shown in Table I together with the level spacings $h\nu_{W-i}$ (all level spacings are equal for a given gas atom in the harmonic oscillator approximation).

The next task is to evaluate the activation energy for re-emission, E_d of Eq. (1). Using the nomenclature of Ref. 1, where E_f is the total energy within the potential well after the collision with the surface,

$$E_d = D - E_f. \tag{8}$$

Combining Eq. (8) with the definition of the thermal accommodation coefficient α, it may be shown that[1]

$$E_d = k\{[(D/k) - T_s]\alpha - T_g(1-\alpha)\}, \tag{9}$$

where T_s and T_g are the surface and gas temperatures, respectively. The quantity E_d is the difference between the vacuum level (energy zero) and the mean *reflected* gas energy, and it may be evaluated using Eq. (9). For room temperature helium, neon, and argon, E_d lies above the energy zero for the surface temperatures of interest ($T_s > 375$ K for the experimental conditions of Ref. 2); thus the *average* reflected helium, neon, and argon atom is not trapped. For a room temperature gas, and surface temperatures of 375, 575, and 775 K, the values of E_d may be found in Table II. Values of E_d allow the calculation of n in Eq. (1) since

$$(n_i + \tfrac{1}{2})h\nu_{W-i} = D_{W-i} - E_{di}, \tag{10}$$

where the i designates the particular rare-gas atom under consideration. The values of n calculated using Eq. (10) may be found in Table II. Once n is known it is possible to calculate the residence time of the *average* trapped atom, τ_a, according to Eq. (1). These results are also shown in Table II along with N, the number of cycles the average reflected (trapped) atom undergoes with the surface tungsten atom. The number of cycles is given by the exponential function in Eq. (1). The time

TABLE III. Reemission parameters of rare-gas atom trapped at the bottom of potential well with a tungsten surface with $T_g = 295$ K.

Gas	T_s (°K)	$\tau_a \times 10^{12}$ (sec)	N (cycles)
He	375	4.85	1.18
	575	4.58	1.12
	775	4.45	1.08
Ne	375	9.20	1.89
	575	7.37	1.52
	775	6.62	1.36
Ar	375	40.5	12.1
	575	17.0	5.08
	775	11.2	3.34
Kr	375	824	278
	575	116	39.2
	775	45.2	15.2
Xe	375	190 000	78 900
	575	3820	1580
	775	572	237

in which the average trapped atom is in the potential well is very short, and also the number of vibrations (cycles) the tungsten–rare-gas atom complex makes is quite small. It thus seems plausible that a rare-gas atom may be trapped in the potential well and still not be reemitted diffusely, i.e., the "trapped" rare-gas atom will not have lost track completely of its incident trajectory. This argument explains, qualitatively perhaps, the reason the calculated trapping probabilities for krypton and xenon are significantly larger than the experimental values.[2]

The residence time with respect to reemission (or desorption) from the bottom of the potential wells ($n = 0$) is much larger, of course, than the values given in Table II. These residence times calculated according to Eq. (1) are shown for comparison in Table III together with the average number of cycles or vibrations N the tungsten–rare-gas complex undergoes prior to reemission of the rare-gas atom.

The arguments presented above give a qualitative rationale for the disagreement between experimental trapping probabilities of the rare gases (krypton and xenon in particular) and the theoretical values calculated according to the square well model.[1] Until more accurate gas–surface interatomic potentials become available, empirical correlations such as those proposed in this paper should be useful in providing some insight into the phenomenon of gas trapping at solid surfaces.

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